

Magnetic Properties of a Quantum Ferrimagnet:

$\text{NiCu(pba)}(\text{D}_2\text{O})_3 \cdot 2\text{D}_2\text{O}$

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Abstract

We report the results of magnetic measurements on a powder sample of $\text{NiCu(pba)}(\text{D}_2\text{O})_3 \cdot 2\text{D}_2\text{O}$ (pba=1,3-propylenebis(oxamato)) which is one of the prototypical examples of an $S=1/2$ and 1 ferrimagnetic chain. Susceptibility(χ) shows a monotonous increase with decreasing temperature (T) and reaches a maximum at about 7 K. In the plot of χT versus T , the experimental data exhibit a broad minimum and are fit to the χT curve calculated for the ferrimagnetic Heisenberg chain composed of $S=1/2$ and 1. From this fit, we have evaluated the nearest-neighbor exchange constant $J/k_B=121$ K, the g-values of Ni^{2+} and Cu^{2+} , $g_{\text{Ni}}=2.22$ and $g_{\text{Cu}}=2.09$, respectively. Applied external field dependence of χT at low temperatures is reproduced fairly well by the calculation for the same ferrimagnetic model.

Extensive studies of one-dimensional systems were prompted by Haldane's theoretical work [1] in 1983 after the initial wave of studies [2,3] in the late 1960s and early 1970s.

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Recently, quantum spin systems with singlet ground states, namely Haldane systems [1] (linear chain Heisenberg antiferromagnets with integer spin values), inorganic spin-Peierls systems [4] and even-leg spin ladder systems, [5] have been studied extensively. In particular, cuprate systems have attracted much attention because of the relation to high T_c superconductors.

In regard to the one-dimensional systems with magnetic ground states, an $S=1/2$ and 1 ferrimagnetic chain has been theoretically investigated recently, [6–9] in addition to some pioneering theoretical works [10,11] published in the 1980s. From the low dimensionality and small spin values in this system, we expect a kind of quantum effect. Theoretical studies show some remarkable features as follows: (1) between two low-lying, gapless and gapped excitation branches, the gapped branch lies higher than that deduced from a conventional spin wave theory. From reliable calculations, [8] the gap (Δ/J) has been evaluated to be 1.767 ± 0.003 where J is the nearest-neighbor exchange constant. The definition of the Hamiltonian will be shown later. (2) The spin correlation length between sublattice moments is extremely short. The length is below unit cell length and can not be evaluated with numerical accuracy. (3) The full magnetization curve up to saturated magnetization is calculated and is obviously different from that for a classical ferrimagnet. [12]

On the other hand, although some candidates for the ferrimagnetic Heisenberg chain composed of spin $1/2$ and 1 exist in real bimetallic substances, [13,14] only preliminary magnetic measurements and comparisons with numerical calculations were made. [13] Thus, we investigate precisely the magnetic properties of an alternating Ni and Cu chain compound $\text{NiCu(pba)(D}_2\text{O)}_3 \cdot 2\text{D}_2\text{O}$ (pba=1,3-propylenebis(oxamato)). In these measurements, we use a deuterated sample because it is of superior quality to a hydrated one, although reason for this remain unclear and we plan to perform neutron scattering measurements on this deuterated sample. The format used in this letter is as follows: in the next section, we discuss the synthesis and crystal structure of $\text{NiCu(pba)(D}_2\text{O)}_3 \cdot 2\text{D}_2\text{O}$. We then report the results of magnetic measurements and of the comparison with numerical calculations for $S=1/2$ and 1 ferrimagnetic Heisenberg chain. Finally, we show the field dependence of χ times T and

compare the experimental data with calculated ones for the same model.

Powder samples of $\text{NiCu(pba)(D}_2\text{O)}_3\cdot 2\text{D}_2\text{O}$ were synthesized according to the procedure reported in ref. 13. $\text{Na}_2[\text{Cu(pba)}]\cdot 6\text{H}_2\text{O}$ was prepared from CuSO_4 , NaOH and 1,3-trimethylenebis(oxamido) [15] which was previously synthesized from ethyl oxamate and 1,3-propanediamine. Then, the title compound was obtained by slow diffusion of aqueous solutions ($\text{D}_2\text{O} > 99.8\%$) of $\text{Na}_2[\text{Cu(pba)}]\cdot 6\text{H}_2\text{O}$ and $\text{Ni(ClO}_4)_2\cdot 6\text{H}_2\text{O}$ in a U-tube. Chemical analysis showed a slight deviation of H content from the ratio in the ideal deuterated sample, but the molecular weight of this sample was only about 1% smaller than that of $\text{NiCu(pba)(D}_2\text{O)}_3\cdot 2\text{D}_2\text{O}$. Crystal structure of $\text{NiCu(pba)(H}_2\text{O)}_3\cdot 2\text{H}_2\text{O}$ has not been analyzed, but that of a similar compound $\text{MnCu(pba)(H}_2\text{O)}_3\cdot 2\text{H}_2\text{O}$ where Mn replaces Ni, has been analyzed. [13] Powder x-ray diffraction patterns of these compounds show that these belong to the same space group. Thus, $\text{NiCu(pba)(H}_2\text{O)}_3\cdot 2\text{H}_2\text{O}$ crystallizes in the orthorhombic system and belongs to the $Pnma$ space group. [13] As shown in Fig. 1, the structure consists of ordered bimetallic chains along the b axis with octahedral Ni^{2+} and square-pyramidal Cu^{2+} ions bridged by oxamato groups. At the apical positions of Ni and Cu, water molecules are bound.

Magnetic measurements were carried out with a SQUID magnetometer (Quantum Design's MPMS-XL7L) at KYOKUGEN in Osaka University. We show in Fig. 2 the dc magnetic susceptibility $\chi (=M/H$ where M and H represent magnetization of the sample and the external magnetic field, respectively) of a powder sample of $\text{NiCu(pba)(D}_2\text{O)}_3\cdot 2\text{D}_2\text{O}$. The susceptibility of $\text{NiCu(pba)(D}_2\text{O)}_3\cdot 2\text{D}_2\text{O}$ increases monotonously with decreasing temperature until about 7 K, at which the susceptibility reaches a maximum. Below 7 K, the long-range order probably occurs due to the interchain couplings.

Figure 3 shows χ times T of $\text{NiCu(pba)(D}_2\text{O)}_3\cdot 2\text{D}_2\text{O}$ as a function of temperature. This plot is familiar to chemists but not to physicists. Therefore, we explain this plot in some details. If a magnetic system is paramagnetic, χT is constant over the whole temperature range. If a magnetic system has a dominant ferromagnetic (antiferromagnetic) interaction, χT increases (decreases) when the temperature is decreased. In Fig. 3, χT decreases when

decreasing the temperature from 300 K, implying that antiferromagnetic coupling exists between the nearest neighbor spins, and reaches a rounded minimum at about 70 K. Then, χT increases and reaches a maximum at about 10 K, and hereafter, when the temperature is decreased further, it decreases rapidly. The increase in χT below 70 K implies that this ferrimagnetic system behaves like a ferromagnetic chain at low temperatures. Interchain (antiferromagnetic) couplings probably give rise to the steep decrease of χT below 10 K. We compare the experimental data with numerical calculations (exact diagonalization method up to five unit cells (ten sites)) for the $S=1/2$ and 1 ferrimagnetic Heisenberg chain. The Hamiltonian of this system in a magnetic field is defined by

$$\mathcal{H} = J \sum_{i=1}^L [\mathbf{S}_i \cdot \mathbf{s}_i + \mathbf{s}_i \cdot \mathbf{S}_{i+1}] - g_S \mu_B H \sum_{i=1}^L \mathbf{S}_i - g_s \mu_B H \sum_{i=1}^L \mathbf{s}_i, \quad (1)$$

where \mathbf{S} and \mathbf{s} are the $S=1$ and $S=1/2$ spin operators, respectively, and g_S and g_s the g -values of the $S=1$ and $S=1/2$ magnetic moments, respectively, and μ_B the Bohr magneton and H the external magnetic field. Here, the periodic boundary condition is imposed, so that $\mathbf{S}_1 = \mathbf{S}_{L+1}$. The solid line in Fig. 3 shows the result of the best fit to the experimental data between 30 K and 150 K. Good agreement between experimental and calculated results is achieved between 30 K and 150 K. Slight deviation at high temperatures may arise from the error enhancement of χT at high temperatures or the omission of the single ion anisotropy term which exists in $\text{Ni}(S=1)$ compounds. From this fit, we obtain the exchange constant $J/k_B=121$ K, $g_S(=g_{\text{Ni}})=2.22$ and $g_s(=g_{\text{Cu}})=2.09$.

Next, we show the magnetic field dependence of χT in Fig. 4. Experimental data of χT at 0.1 T (open squares), 1 T (open triangles) and 7 T (open circles) are plotted in the upper panel. Experimental data at 0.1 T and 1 T have a similar tendency, but χT at 7 T at low temperatures deviates significantly from the others. This behavior is reproduced in the calculation shown in the lower panel. Here, the designated H/J figures represent those of $g\mu_B H/J$ with $g=2.0$ and $J/k_B=121$ K, and magnitudes of χT are calculated for the above Hamiltonian using $g_S=2.22$ and $g_s=2.09$. The low temperature behavior of χT at 7 T implies that the Néel order tends to be fixed and the ferromagnetic fluctuation of magnetic

moments is suppressed by the external field.

In conclusion, magnetic properties of alternating Ni and Cu chain compound $\text{NiCu(pba)(D}_2\text{O)}_3 \cdot 2\text{D}_2\text{O}$ were investigated by magnetic susceptibility measurements. From comparison with a numerical calculation for the ferrimagnetic Heisenberg chain composed of $S=1/2$ and 1, we have obtained the values of the exchange constant and the g -values of Ni and Cu. Field dependence of χT at low temperatures has been reproduced by similar calculations in magnetic fields.

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FIGURES

FIG. 1. Crystal structure of $\text{NiCu(pba)(H}_2\text{O)}_3 \cdot 2\text{H}_2\text{O}$. Alternating Ni and Cu chain runs along the b axis. Hydrogen atoms are omitted for clarity.

FIG. 2. Temperature dependence of the susceptibility($=M/H$) of a powder sample of $\text{NiCu(pba)(D}_2\text{O)}_3 \cdot 2\text{D}_2\text{O}$. Inset: Susceptibility of $\text{NiCu(pba)(D}_2\text{O)}_3 \cdot 2\text{D}_2\text{O}$ at low temperatures. We see the cusp around 7 K where the long-range order probably occurs.

FIG. 3. χT versus temperature plot of $\text{NiCu(pba)(D}_2\text{O)}_3 \cdot 2\text{D}_2\text{O}$. The solid line shows the fit to a numerical calculation for the ferrimagnetic Heisenberg chain composed of $S=1/2$ and 1.

FIG. 4. Magnetic field dependence of χT of $\text{NiCu(pba)(D}_2\text{O)}_3 \cdot 2\text{D}_2\text{O}$. Upper panel shows the experimental data for the designated applied field. The values of H/J represent the ratios of $g\mu_B H$ to J with $g=2.0$. In the lower panel, field dependence of calculated χT corresponding to H/J values in the upper panel is shown.

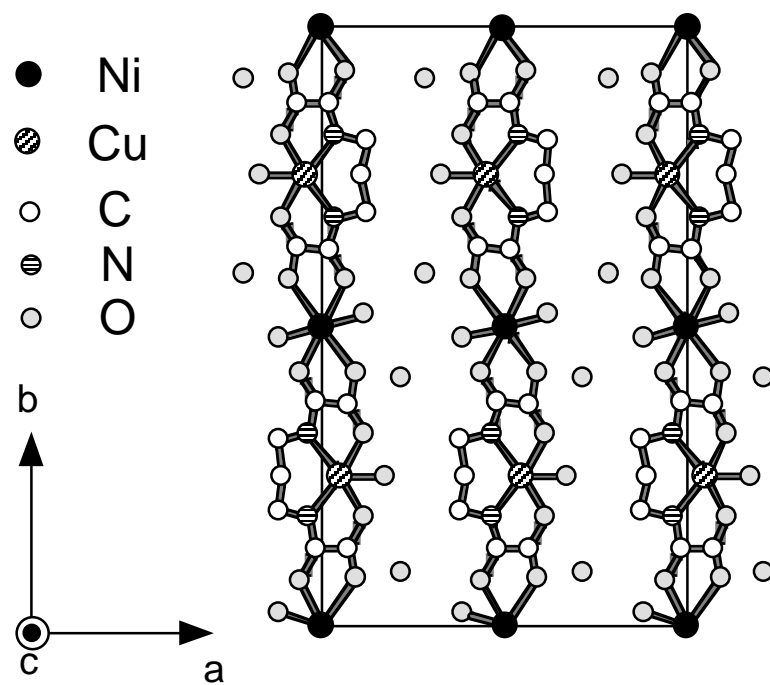


Fig.1 Hagiwara et al.

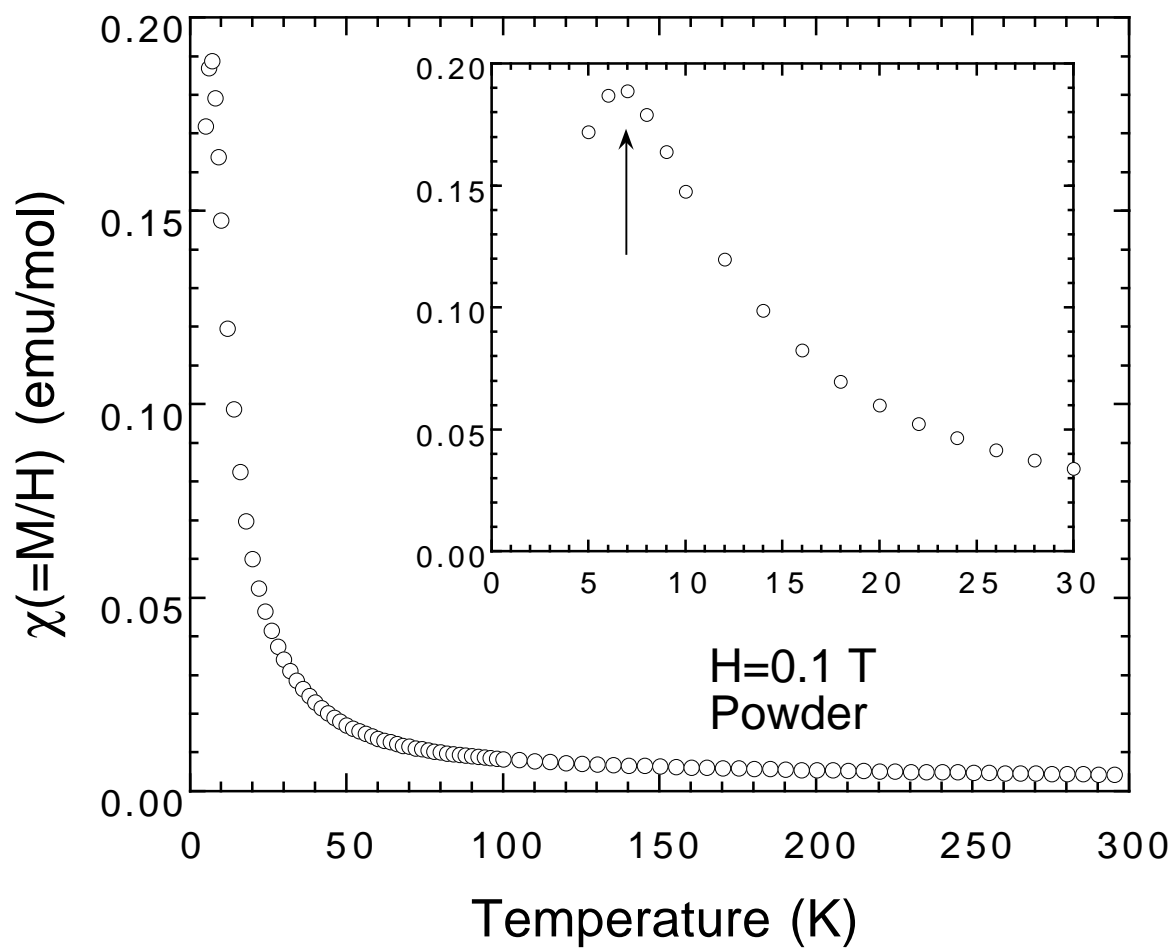


Fig.2 Hagiwara et al.

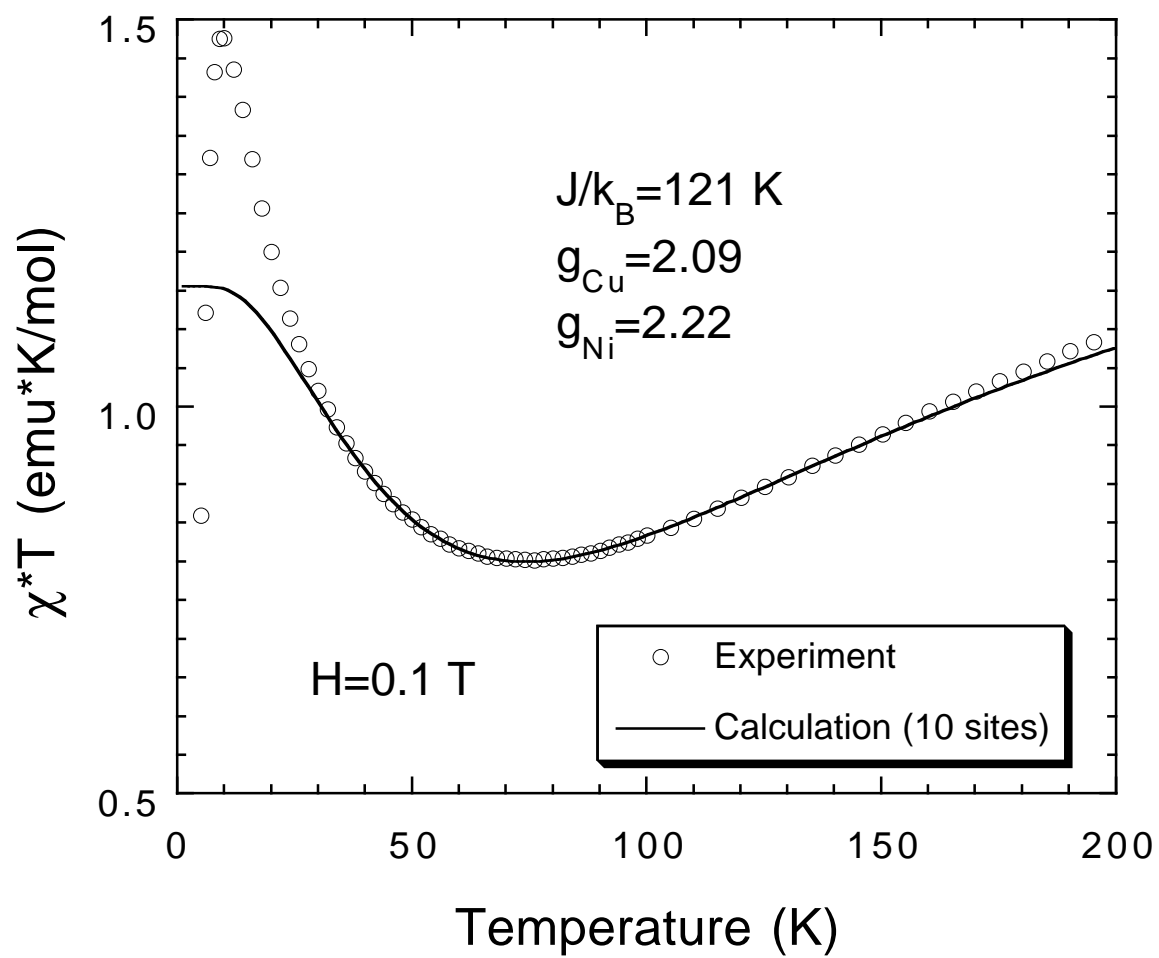


Fig.3 Hagiwara et al.

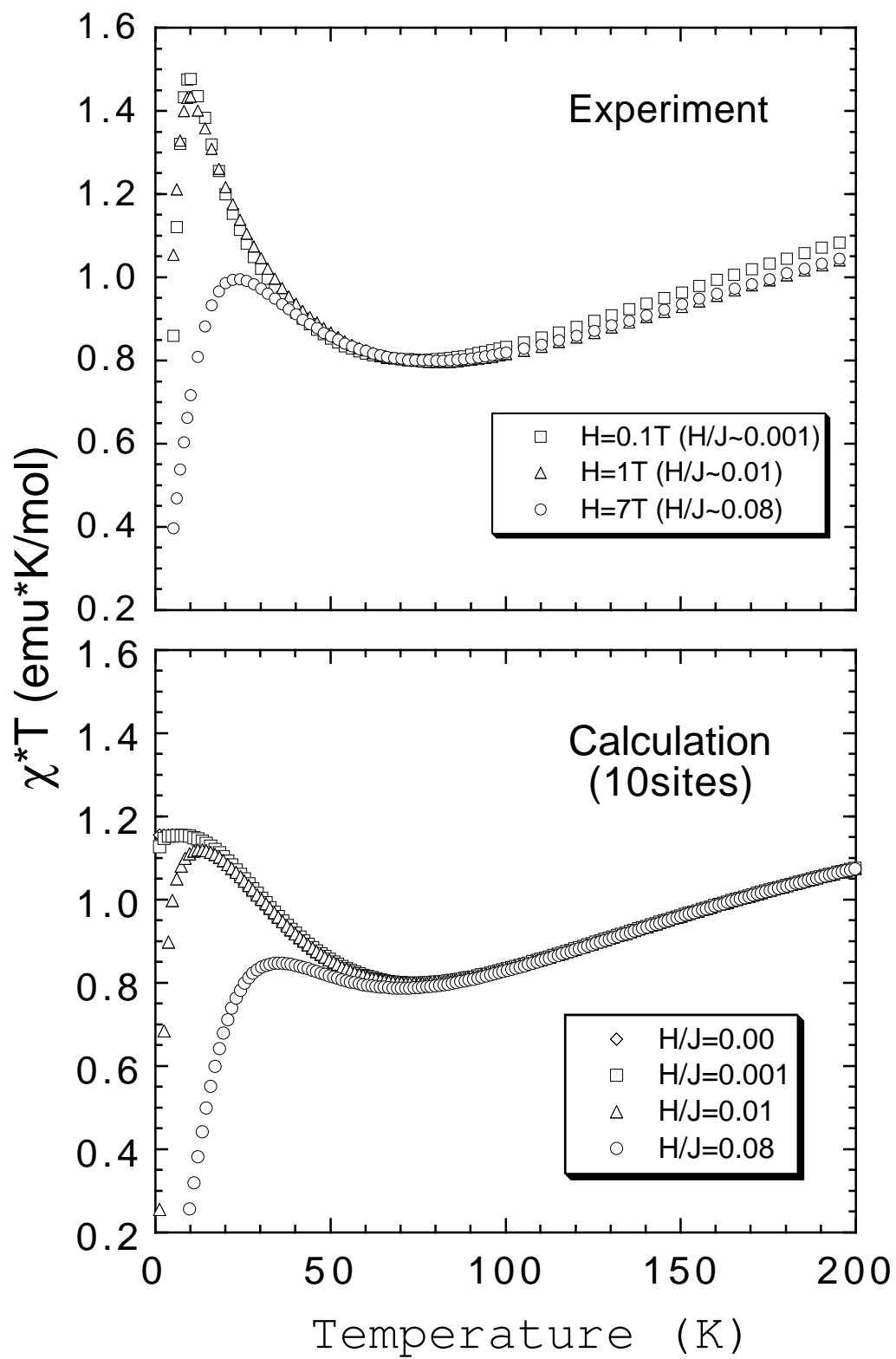


Fig.4 Hagiwara et al.